THERMAL CONDUCTIVITY AND HEAT TRANSFER IN COAL SLAGS

K C MILLS

National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK

1. INTRODUCTION

During the gasification of coal, both molten and solid slags are formed in the
converter, and the heat transfer within the gasification chamber is governed
to a large extent by the thermal properties of the slag phase. Thus in order to
carry out either heat balance or modelling calculations it is necessary to have
reliable data for the thermal properties of both solid and liquid coal slags.
However, the thermal transfer mechanisms in high temperature processes involving
slags are exceedingly complex since heat can be transported by convection, radi-
ation and thermal conduction. The total thermal conductivity (k_{eff}) is, in turn,
made up from contributions from (i) the thermal ("phonon") conductivity, k_C, (ii)
radiation conductivity, k_R and (iii) electronic conductivity, k_{el}. Heat balance
calculations must take account of all these thermal transport mechanisms; con-
sequently it is necessary to study the effects of the various mechanisms for not
only do they determine the heat transfer in the gasifier, but they can also
critically affect the experimental values derived for the thermal conductivity of
the slag. Hence the factors affecting the thermal conductivity of slags will be
examined and their effect on the various methods available for the measurement of
thermal conductivities will be assessed. Finally, experimental data for the
thermal conductivity of slags, glasses and magmas will be evaluated to provide a
reliable data base for the thermal conductivity of slags, and to determine the
likely effects of variations in chemical composition upon values for coal slags.

2. THERMAL CONDUCTION MECHANISMS

2.1 Thermal "phonon" conductivity (k_C)

Heat is transferred through a medium by phonons, which are quanta of energy assoc-
iated with each mode of vibration in the sample. This mode of conduction is thus
referred to as thermal, phonon or lattice conduction. Scattering of the phonons
causes a decrease in the thermal conductivity and hence the conductivity is sens-
itive to the structure of the sample. Scattering of the phonons can occur by
collisions of the phonons with one another, or by impact with grain boundaries or
crystal imperfections, such as pores. Thus a low-density, highly-porous material
will have a low thermal conductivity. In glassy, non-crystalline materials it has
been suggested [1] that thermal conductivity decreases as the disordering of the
silicate network increases.

2.2 Radiation conductivity (k_R)

Measurements of the thermal conductivity of glasses were found to be dependent upon
the thickness of the specimens used, and this is shown in Figure 1. This behaviour
was ascribed to the contribution from radiation conductivity, k_R, which can occur
in semi-transparent media like slags and glasses. Radiation conductivity occurs
by a mechanism involving absorption and emittance of radiant energy by various
sections through the medium. Consider a thin section in the slag, radiant energy
absorbed by the section will cause it to increase in temperature and consequently
radiant heat will be emitted to cooler sections. This process can occur right
through the medium and it is obvious that the energy transferred in this way will
increase with increasing number of sections (ie increasing thickness) until the
point where k_R attains a constant value. At this point the slag is said to be
"optically thick", and this is usually considered to occur when $\alpha d > 3.5$, where α
and d are the absorption coefficient and thickness of the slag, respectively.

At high temperatures, radiation conductivity can be the predominant mode of con-
duction, eg in glassmaking more than 90% of the total conductivity occurs by
radiation conduction. The radiation conductivity can be calculated for an
optically-thick sample if steady-state conditions apply and if it is assumed that
the absorption coefficient of the medium, α, is independent of wavelength, λ, ie
grey-body conditions obtain. For these conditions k_R can be calculated by use of
equation 1), where σ and n are the Stefan-Boltzmann constant and refractive index,
respectively.

$$k_R = \frac{16\sigma n^2 T^3}{3\alpha} \cdot \qquad\qquad 1)$$

Values of k_R cannot be calculated for optically-thin samples ($\alpha d < 3.5$) and for some
measurement techniques involving non-steady state conditions. Thus it is obvious
that reliable values of thermal conductivity can only be obtained when either k_R
is negligible, or where it can be calculated reliably for optically-thick conditions.

Absorption coefficient (α)

The absorption coefficient is a very important parameter, as it determines (i) the
magnitude of k_R (equation 1) and (ii) the thickness at which a slag becomes
optically thick ($\alpha d > 3.5$). Hence increasing α has the effect of decreasing k_R and
decreasing the depth at which a slag becomes optically thick. If a particular slag
sample were optically thin, these two factors would operate in opposition to one
another.

The absorption coefficient is markedly dependent upon the amounts of FeO and MnO
present in the slag [2]; although Fe_2O_3 absorbs infra-red radiation, its effect on
α is much less pronounced than that of FeO. An empirical rule has been derived[2]
for glasses containing less than 5% FeO, the absorption coefficient at room temp-
erature is given by the relationship, $\alpha = 11.$ (% FeO).

A basic assumption adopted in deriving equation 1) was that α was independent of
wavelength; however, in practice the spectral absorption coefficient (α_λ) varies
with the wavelength (λ) as shown in Figure 2 for a glass containing ca. 5% FeO.
It can be seen from this figure that there is strong absorption by FeO at ca. 1 μm
and by SiO_2 at ca. 4.4 μm. At high temperatures this restricts absorption by the
slag to a "window", in the wavelength range 1-4.4 μm. However, even within this
wavelength band there is some variation in α_λ and the average absorption coefficient,
α_m, is determined by weighting of the α_λ values.

The average absorption coefficient, α_m, can be affected by temperature in two differ-
ent ways. Firstly, the absorption spectrum, ie, (α_λ), can change markedly with temper-
ature and consequently alter the value of α_m. Secondly, even if the absorption
spectrum is unaffected by temperature, α_m would continue to be a function of temper-
ature because the wavelength distribution used in deriving α_m is itself a function
of temperature. This can be seen in Figure 3 where the fraction of total energy
emitted in the "window" 1-4.4 μm constitutes 61.1%, 79.5% and 81.9% of the total
energy emitted at 1073K, 1573K and 1773K, respectively. In a similar manner, the
various α_λ values of the spectrum will have to be weighted differently in the cal-
culation of α_m for the three temperatures in question.

It can be seen from Figure 2 that α_m increases with increasing temperature, and
similar behaviour has been observed in rocks and minerals [4,5,6]. By contrast,
the absorption coefficients (α_m) of amber glass have been found to decrease with
increasing temperature.

Extinction coefficient (E)

In solids, radiant energy can be scattered by grain boundaries, pores and cracks
in the material. In these cases, it is necessary to use the extinction coefficient
(E) which is given by the relationship $E = \alpha + s$, where s is the scattering co-
efficient.

2.3 Electronic conductivity (k_{el})

It has been reported that glasses which contain significant concentrations of Fe^{2+} ions behave in a similar manner to semi-conductors and hence thermal conduction via conduction electrons, holes, etc. could be significant, according to Fine et al[7]. Little is known of this mechanism in relation to the heat transfer in slags and consequently the contribution of k_{el} to the measured thermal conductivities has been ignored in this review.

2.4 Total thermal conductivity (k_{eff})

In practice, the radiation and conduction contributions to the heat flux (Q) are interactive, and the interpretation of the combined conductive-radiative heat trans-fer is exceedingly complex. Various models have therefore been proposed to simplify the theory of the heat transfer process. One widely-used model is the diffusion approximation which assumes that the heat flux (Q) is given by equation 2), where k_{eff} is the effective thermal conductivity and is defined by equation 3) where x is the distance. Gardon [8] has pointed out that this model only applies strictly when (i) k_R is small and (ii) α d $>$ 8.

$$Q = -k_{eff} \, (dT/dx) \qquad\qquad 2)$$

$$k_{eff} = k_c + k_R \qquad\qquad 3)$$

3. EXPERIMENTAL METHODS FOR DETERMINING THERMAL CONDUCTIVITY

The experimental methods available for measuring thermal conductivities are sum-marised below; more detailed reviews of the experimental techniques are available elsewhere [3,9,10,11]. The techniques can be divided into three classes: (i) steady-state methods, (ii) non-steady state methods, and (iii) indirect methods for the determination of k_R. The steady-state methods usually yield k_{eff} values and the non-steady state techniques usually produce thermal diffusivity (a_{eff}) values, which can be converted to thermal conductivity values by use of equation 4), where ϱ and Cp are the density and heat capacity of the slag.

$$k = a. \, Cp. \varrho \qquad\qquad 4)$$

3.1 Steady-state methods

These methods all yield k_{eff} values provided that the specimen is optically thick.

In the linear heat-flow method two disc-shaped specimens are placed on either side of an electrically-heated plate and the temperature profiles across the samples are monitored by thermocouples sited on both faces of the specimens. The apparatus is well insulated to minimise heat losses. In some versions of this method, the total heat fluxes passing through the samples are determined by calorimeters in contact with the specimens. When high-temperature measurements are required, this technique is usually operated as a comparative method [12].

In the radial heat-flow method the specimen is in the shape of a hollow cylinder, which is sited in the annulus between two coaxial cylinders with the internal cylinder acting as a radial heat source [13]. The temperature profile across the specimen is determined by thermocouples placed on the inside walls of the two cylinders. This method requires a large isothermal zone in the furnace, which is difficult to achieve at high temperatures. When this technique is used for measure-ments on liquids it is prone to errors from convective heat transfer.

3.2 Non-steady state methods

In the radial wave method the slag is placed in a cylindrical crucible sited in the isothermal zone of a furnace, and thermocouples are located on the walls and along the geometric axis of the crucible (the slag). The outside wall of the

of the crucible is then subjected to a sinusoidal variation of temperature and the variation in temperature of the central thermocouple is monitored. There is a phase shift between the input and output which is related to the thermal diffusivity of the slag. In the modification of this apparatus used by Elliott and co-workers[7,14] the periodic variation in temperature is produced in a wire running along the central axis of the cylindrical crucible, and the phase shift is measured in the signal of the thermocouples sited on the walls of the crucible. The thermal diffusivity values obtained with this method may be vulnerable to errors arising from convective heat transfer.

In the modulated beam method the specimen is in the form of a disc, which is maintained at a constant temperature, whilst the front face of the disc is subjected to a laser beam which produces a periodic variation in temperature of constant frequency. The phase shift between this input and the signal from a temperature sensor in contact with the back face is determined. By carrying out measurements at two or more frequencies, Schatz and Simmons[6] were able to derive values of both a_{eff} and the extinction coefficient. If this method were applied to measurements in liquids, it too would be prone to errors caused by convection.

The laser pulse method[15,16] when applied to solids uses a disc-shaped slag specimen coated with metallic films on both planar surfaces. A laser pulse is directed on to the front face of the specimen and the temperature of the back face is monitored continuously. The maximum temperature rise of the back face (ΔT_{max}) usually occurs after ca. 10 seconds, and a_{eff} may be computed from the time taken ($t_{0.5}$) for the back face to attain a temperature rise of (0.5 ΔT_{max}). The method has also been applied to measurements on liquid slags[15,17] which were contained in Al_2O_3 or BN crucibles. The major advantage of this technique is that the short duration of the experiment minimises the errors due to convection. The major disadvantage is that the maximum specimen thickness is about 4 mm, and consequently optically-thick conditions only apply when the extinction coefficient is greater than 9 cm^{-1}. A second disadvantage is that the laser pulse method is a transient technique and k_R cannot be calculated by equation 1), which is applicable to steady-state conditions; at the present time no formulae exist for the calculation of k_R for this method. Thus this technique is most useful when applied to specimens which have (i) very small values of αd (ie $\alpha d \ll 3.5$) where $a_{eff} \simeq a_c$, or (ii) large extinction coefficients where k_R is negligible and thus $a_{eff} = a_c$.

The line source method is also a transient technique and is the standard method for measuring the thermal conductivities of liquids at lower temperatures. In the high-temperature versions, this method consists of a fine Pt wire (ca. 0.1 mm dia) which is sited centrally in a crucible of molten slag. This wire acts as both heating element and temperature sensor. When an AC or DC current is applied to the wire, the temperature rise of the wire (ΔT) is monitored continuously during the heating period (ca. 1 second). A linear relationship exists between ΔT and ln (time), the slope of which is proportional to (1/k). This method has the advantage that convectional heat transfer is eliminated (if convection does occur it results in a non-linear ΔT-ln (time) plot and can therefore be readily detected). Routines are available for calculating the value of k_R for optically-thick conditions[18]; however, de Castro et al.[19] have recently proposed that k_R is negligible in the values of k_{eff} measured by this technique at ambient temperatures (ie $k_R \simeq 0$, $k_{eff} = k_c$). There is evidence to support the view that $k_R \simeq 0$, as measurements made with this technique at higher temperatures[20,21,22] yield much lower values of k_{eff} for slags than those obtained by steady-state techniques. Furthermore, Powell and Mills[23] have pointed out that the thermal conductivity data for molten salts become more consistent if k_R is taken to be zero in the various line source determinations.

3.3 Indirect measurements of k_R

The absorption (or extinction) coefficient can be determined by measurement of the optical transmissivity (γ) of the slag as a function of wavelength; the absorption coefficient (α) is given by equation 5), where d is the thickness of the specimen.

Measurements at high temperatures are carried out by using

$$\alpha_\lambda = - \ln(\gamma_\lambda)/d \qquad \qquad 5)$$

an assembly of mirrors to direct a beam of radiation of known frequency on to a disc-shaped specimen sited in a tube furnace. The transmitted beam is diverted into an infrared spectrophotometer where the transmissivity is determined. Blazek and Endrys[3] have reported that k_R values for glasses calculated from absorption coefficient data are in good agreement with values of $(k_{eff} - k_c)$ determined experimentally.

3.4 Summary of experimental limitations

(i)   It is important to ensure that the thermal conductivity measurements on semi-transparent media should be carried out with optically-thick specimens, as k_R cannot be calculated for optically-thin conditions. It is recommended that absorption coefficient measurements should also be carried out to determine the slag thickness required to produce an optically-thick specimen.

(ii) The non-transient techniques are prone to errors due to convectional heat transfer.

(iii) At the present time no reliable routines are available for calculating the k_R contribution to the overall thermal conductivity measured in transient techniques; there is some evidence to suggest that k_R is negligible in measurements obtained by the line source method.

4.   REVIEW OF THE EXTANT DATA FOR SLAGS

There is a paucity of data for coal slags; it is therefore necessary to study a much broader range of slags in order to determine the effects of compositional change on the thermal conductivity of the slag. One problem continually encountered is that the distribution of Fe in slags between (Fe^{3+}), (Fe^{2+}) and free iron is not reported, and this can have a marked effect on the absorption coefficient and consequently k_R. Furthermore, the ratio of $((Fe^{2+})/(Fe^{3+}))$ is known to vary with (i) temperature, (ii) $p(O_2)$ and (iii) the composition of the slag, (Fe^{2+}) increasing with increasing SiO_2 and TiO_2, and decreasing CaO and Na_2O.

4.1   CaO + SiO_2 + FeOx

Fine et al[7] determined the absorption spectra at room temperature of three slags containing 0, 7 and 14% FeO (Figure 4). The absorption coefficients of the slags containing 7 and 14% FeO will probably increase with increasing temperature as the (Fe^{2+}/Fe^{3+}) ratio increases with increasing temperature. An increase in α with increasing temperature can also be seen in Figure 2. Fine et al[7] used the radial wave method to determine a_{eff} of solid and liquid slags containing 0 to 25% FeO; their results are summarised in equation 6), where B represents the basicity, ie (CaO/SiO_2) ratio and T is the temperature in (°C).

$$a_{eff} = 10^{-7}(1.5 - 0.5 B) + 1.8 \times 10^{-6} \frac{(T/1500)^3}{(\%FeO)^{0.8}} \quad m^2s^{-1} \qquad 6)$$

This equation indicates that increasing the FeO content results in a reduction of a_{eff}; this behaviour is due presumably to the increase in α and hence the consequent decrease in k_R with increasing FeO content. However, Nauman et al[24] using the same experimental technique as Fine et al[7] obtained the k_{eff} – (% FeO) relationship shown in Figure 5 for molten slags with high FeO contents. The density of slags are known to increase with increasing (FeO$_x$, MnO) content, thus $k(= a.C_p.\rho)$ would be expected to increase as the level of FeO increases[25]. However, calculations have shown that this increase in k would be ca. 30%, and this alone would not account for the increase in k shown in Figure 5. Thus it must be concluded that FeO additions do increase the thermal diffusivity of the

system. In these slags with high FeO content, the absorption coefficient must be very high and thus k_R must be negligible and $k_{eff} = k_c$.

4.2 CaO + Al$_2$O$_3$ + SiO$_2$

Measurements on solid slags have been reported by Kingery[12](comparative linear heat-flow method), Osinovskikh[25] and Susa et al[21](line source method), and for the liquid phase by Susa et al[21] and Ogino et al[13](radial heat-flow); the results are summarised in Figure 6. The data recorded by Osinovskikh[25] appear to be too low, but there is some measure of agreement between the data obtained for the liquid near the liquidus temperature (T_{liq}). However, the reported, thermal conductivity values diverge as the temperature increases, and this is possibly due to the negligible contribution of k_R in the line source measurements[20] and the effects of k_R and convective heat transfer on the value due to Ogino[13]. The value due to Kingery[12] for the compound $3Al_2O_3 \cdot SiO_2$ is appreciably higher than that for the slags of the ternary system.

4.3 MgO + Al$_2$O$_3$ + SiO$_2$

Values for the various binary compounds occurring in this system have been reported by Rudkin[26] and by Kingery[12] (comparative linear heat-flow method), and by Schatz and Simmons[6] (modulated beam method) for temperatures up to 1300 °C; there is excellent agreement between the values due to the latter two groups of workers. Schatz and Simmons[6] reported that extinction coefficient of $2MgO \cdot SiO_2$ increases from 5 cm^{-1} at 270 °C to 25 cm^{-1} at 1300 °C.

4.4 Na$_2$O + SiO$_2$

Susa et al[21] (line source method) reported thermal conductivity data for solid and liquid slags for three compositons; the single value obtained by Ogino et al[13] (radial heat-flow method) is in reasonable agreement with these data.

4.5 Glasses

Blazek and Endrys[3] have reviewed the thermal conductivity data for glasses. The lattice thermal conductivity, k_c, for glasses is relatively unaffected by composition and was found to increase with temperature from $1 Wm^{-1}K^{-1}$ at 25 °C to $2.7 Wm^{-1}K^{-1}$ at 1300 °C. However, the radiation conduction is frequently the dominant mode of heat conduction in glasses at high temperatures.

4.6 CaF$_2$-based slags

Extinction coefficients have been reported (1.3 cm^{-1} for 1000-1300 °C) by Keene and Mills[27], and absorption coefficients (1.3 cm^{-1}) for the liquid state by Mitchell and Wadier[22].

The thermal conductivity values for polycrystalline (optically-thick) CaF$_2$ obtained by Kingery[12] (comparative linear flow method) and by Taylor and Mills[16] are in reasonable agreement (Figure 7). However, there is an appreciable discrepancy between the values of k obtained by the line source method[20-22] and the single value due to Ogino et al[13] (radial heat source method).

The reason for the discrepancy probably lies in the magnitude of the k_R values measured in the two experiments, as k_R is probably negligible for the line source technique, in contrast to the steady-state method where k_R would be appreciable despite the fact that the sample was probably optically thin ($\alpha d \simeq 0.8$).

4.7 TiO$_2$-based slags

Values of thermal diffusivity, a_{eff}, of ca. 3×10^{-7} m^{2}s^{-1} have been reported by Raflovich and Denisova[28] for slags based on TiO$_2$ (>45%) and SiO$_2$ with small

amounts of Al_2O_3 and Fe_2O_3. The data reported by Osinoskikh et al[25] for slags with less than 15% TiO_2 are much lower, this is probably due to the high porosity of the sample used.

4.8 Continuous casting slags

These slags have the approximate composition ($CaO = SiO_2 = 35\%$; $Al_2O_3 \simeq 7\%$; Na_2O (4-15%) and CaF_2 (5-8%). Olusanya[29] has reported that the absorption co-efficients lie in the range (0.5 - 5 cm^{-1}) and thus k_R could be appreciable in these slags. Values for a_{eff} were obtained for ten glassy-slags by Taylor and Mills[30] (laser pulse method) which lay between 4 and 5 x 10^{-7} m^{2}s^{-1} (Figure 8); these slags were optically thin ($\alpha d = 0.4$) and thus we might expect k_R to be small and $k_{eff} \simeq k_c$. Some crystallisation of the samples occurred at temperatures above the glass temperature in these experiments, and this resulted in an initial decrease in a_{eff}, which was subsequently followed by an increase in the thermal diffusivity. Taylor and Mills reported that a_{eff} of a crystallised specimen had a value of 6 x 10^{-7} m^{2}s^{-1}, which is higher than that of the glassy specimens; the crystalline samples would have a higher extinction coefficient and thus k_R would be low and hence $a_{eff} = a_c$. Thermal conductivity values for the liquid phase have been obtained by Nagata et al[31] and by Powell et al[32] (line source method), and by Taylor and Edwards[17] (laser pulse method) and by Ohmiya et al (33) interpretation of thermal flux data). As can be seen from Figure 8, the results from the line source technique are lower than the other data, and this probably reflects the fact that k_R is negligible in the line source experiements. The increase in k_{eff} observed by Taylor and Edwards[17] above the solidus temperature is probably due to the decrease in α (and increase in k_R), as liquid is formed from crystallised slag.

4.9 Blast furnce slags

Values of k_{eff} have been reported by Ischenko[34] and by Vargaftik and Oleschuk[35] for temperatures in the range (200-1000 °C). The values cited are lower than those reported for other slags, which is presumably due to the high porosity of the samples used by these workers.

4.10 Rocks and Minerals

Absorption and extinction coefficients for several rocks and minerals[4,5,6] were found to increase appreciably at high temperatures, eg α_M (peridot) increases from 0.5 cm^{-1} at 25 °C to 4.3 cm^{-1} at 1240°C. Values of k_{eff} (or a_{eff}) have been recorded by Kingery[12], by Kawada[36] (comparative linear flow method), by Murase and McBirney[37] (radial heat flow), and Schatz and Simmons[6] (modulated beam method). The results are given in Figure 9, and Schatz and Simmons[6] reported that for forsterite and olivine at 1300 °C, approximately half of the measured k_{eff} value was due to the contribution of k_R. There is good agreement between the results reported by Kingery[12] and by Schatz and Simmons[6] for k_{eff} of forsterite. The values of k_{eff} reported by Murase and McBirney[37] are appreciably lower than those reported by other investigators, which may indicate systematic errors in the method, or may merely be due to the higher SiO_2 content of the samples studied by Murase and McBirney. The sharp increase in k recorded above 1100 °C for some samples probably indicates the onset of melting, which causes the extinction coefficient to decrease and hence k_R to increase appreciably. It is noticeable that Kawada[36] recorded no marked increase in k_{eff} for dunite (DU), which has an FeO content of 13% and where k_R would be negligible.

4.11 Coal slags

The experimental details of various investigations concerned with these slags are summarised in Table 1. The results are presented in Figure 10; only the upper and lower a-(T) curves reported by Gibby and Bates have been plotted.

The absorption coefficients of these slags are probably quite high, as they contain appreciable levels of FeO and free Fe. Thus the radiation contribution, k_R, will

be relatively small. There is good agreement between the results of the investigations when the appreciable differences in the composition of the slags is taken into account. Gibby and Bates[15] reported that for solid slags the value of a_{eff} varied appreciably from run to run and appeared to be dependent upon the thermal history of the sample. This behaviour was attributed to the crystallinity of the sample and the fact that a_{eff} (crystalline) $>$ a(glass), which is in agreement with the observations on continuous-casting slags. Gibby and Bates[15] also observed that K_2O additions resulted in a decrease in a_{eff} up to 900 °C, and that the a_{eff}-($\bar{T}$) relationship showed a sharp inflection around 950 °C, which was attributed to the crystallisation of the slags.

These workers also reported that a_{eff} appeared to decrease with increasing SiO_2 content or with the ratio $(SiO_2/(SiO_2 + Fe_2O_3 + MgO + CaO))$. This implies that k_C is probably dependent upon the structure of the silicate slag, and thus it should be possible to build up a reliable model for the estimation of k_C in due course. However, it is also possible that the decrease in a_{eff} with increasing SiO_2 content may simply reflect the lower fraction of crystalline phase present in the slag.

5. DISCUSSION

The thermal conductivity data for slags, magmas and glasses have been collated in Figure 11. It can be seen that k_{eff} values for solid coal slags are similar to those for slags from the systems $CaO + Al_2O_3 + SiO_2$ and $CaO + SiO_2 + FeO$ and for those used in continuous casting. Thus it would appear that the chemical composition of the slag has little effect on the values of k_{eff}; however, certain oxides (eg SiO_2, CaO) could exert some influence on the conductivity by altering the crystallinity of the slag. Furthermore, the radiation conduction will also be affected by the crystallinity of the sample as the extinction coefficient will be high for crystalline materials.

It is more difficult to evaluate the thermal conductivity of molten slags, although the data obtained for coal slags[15] and for slags of the system $CaO + FeO + SiO_2$ [7][14] indicate that k_{eff} for the liquid near the melting-point is similar to that for the solid phase . It is noticeable that the k_{eff} values obtained for liquid slags by the line source method are considerably lower than the values obtained with other techniques. It is possible that the line source method is prone to systematic errors when applied to molten slags, but a more likely explanation is that the k_R is negligible in these experiments. As coal slags contain relatively high levels of $(FeO + Fe_2O_3)$, it would be expected that the absorption coefficient of the slag would be high and that the k_R contribution would be small. However k_R increases dramatically with temperature and even a slag with a relatively high absorption coefficient of 100 cm^{-1} would give rise to a contribution of k_R of 0.4 Wm^{-1}K^{-1} at 1800 K.

However as the absorption coefficient is very dependent upon the (Fe^{2+}) concentration the value of k_R will be dependent upon the various factors affecting the (Fe^{2+}/Fe^{3+}) ratio in the slag viz. the ratio increases with (i) increasing temperature (ii) decreasing p (O_2) (iii) increasing SiO_2 and TiO_2 contents and decreasing CaO, Na_2O and K_2O contents in the slag. This review has revealed the urgent need for absorption coefficient data for coal slags at high temperatures and for information relating the absorption coefficient to the FeO content of the slag.

The heat transfer process in the coal gasifier can also be affected by the layer of slag which lines the walls of the gasifier. Recently, Grieveson and Bagha [38] have developed a simple experiment for measuring the thermal flux (Q) in various slags used in the continuous casting of steel. A water-cooled, copper finger is lowered into a crucible containing molten iron covered with a layer of slag and a layer of solidfied slag forms around the cold finger. The thermal flux is determined by measuring the

temperature rise of the cooling water flowing through the copper finger. It was found that the heat flux was related to (i) the thickness of the slag layer and (ii) the thermal resistance of the Cu/slag interface. The thickness of the slag layer is, in turn, dependent upon the viscosity of the slag and upon other factors determining the "melt back" of the slag layer. Grieveson and Bagha [38] observed that the thermal resistance of the Cu/slag interface appeared to be related to (i) the mineralogical constitution of the slag and (ii) the strength of the adhesion between the copper and the slag eg. Q (glass from $CaO.SiO_2$ field giving good Cu/slag adhesion) $>$ Q (glass from $CaO.Al_2O_3.2SiO_2$ phase field with poor Cu/slag adhesion). Thus relatively simple experiments like these simulation tests can provide us with a valuable insight into the factors affecting heat transfer mechanisms occurring in industrial processes.

CONCLUSIONS

(i)   Experimental data for the thermal conductivities of slags must be carefully analysed to establish the boundary conditions of the experiment (eg. optical thickness of the specimen, magnitude of k_R etc.) This evaluation of the data allows one to determine the suitability of a specific thermal conductivity value for subsequent use in heat balance calculations for the gasifier.

(ii)   The thermal conductivities of coal slags are not very dependent upon the chemical composition of the slag.

(iii)   The thermal conductivity of a slag is dependent upon the degree of crystallization and consequently upon the thermal history of the specimen; the thermal conductivity of the crystalline phase is greater than that of the glassy phase.

(iv)   The radiation conduction, k_R, is principally determined by the magnitude of the absorption (or extinction) coefficient. As the absorption coefficient of the slag is largely dependent upon the (Fe^{2+}) concentration in the slag, it will also be dependent upon the factors affecting the (Fe^{2+}/Fe^{3+}) ratio viz, temperature, $p(O_2)$ and the SiO_2, CaO and Na_2O contents of the slag.

(v)   Experimental data are required for the absorption coefficients of coal slags at high temperatures so that the relationship between α_m and the FeO content can be established.

(vi)   Heat transfer in the coal gasifier will be partially dependent upon the thermal resistance of the slag/wall interface and this, in turn, will be dependent upon the mineralogical constitution of the slag adjacent to the wall.

ACKNOWLEDGEMENTS

REFERENCES

(1)   AMMAR, M M., GHARIB, S, HALAWA, M M, E L BADRY, K, GHONEIM, N A and E L BATAL, H A.   J. Non-Cryst. Solids 1982, 53, 165.

(2)   STEELE, F N and DOUGLAS, R W. Phys. Chem. Glasses 1965, 6, 246.

(3)   BLAZEK, A and ENDRYS, J. Review of thermal conductivity data in glass, Part II Thermal conductivity at high temperatures published Intl. Commission on Glass, 1983.

(4)   FUKAO, Y., MITZUTANI, H. and UYEDA, S.   Phys. Earth Planet Interiors
        1968, 1, 57.

(5)   ARONSON, J R, BELLOTI, L H ., ECROAD, S W, EMSLIE, A G., MCCONNEL, R K
        and THUNA, P C von. J Geophys. Res.   1970, 75, 3443.

(6)   SCHATZ, J F and SIMMONS, G.   J. Geophys. Res.   1972, 77, 6966.

(7)   FINE, H A; ENGH, T, and ELLIOTT, J H; Metall. Trans B, 1976, 7B, 277.

(8)   GARDON, R; paper presented at 2nd Intl. Thermal Conductivity Conference,
        Ottawa, 1962, 167.

(9)   GARDON, R Review of thermal conductivity data in glass, Part 1 Thermal
        conductivity at low and moderate temperatures published Intl. Commission
        on Glass, 1983.

(10)   TOULOUKIAN, Y S , POWELL, R W, H O, C Y and KLEMENS, P G.   Thermophysical
        Properties of Matter, volumes 1 (1970) and volume 10 (1973) published by
        IFI/Plenum, New York

(11)   TYE, R P, Thermal conductivity, volumes 1 and 2, 1969, published by
        Academic Press, New York.

(12)   KINGERY, W D, FRANCL, J, COBLE, R L and VASILOS, T.   J. Amer. Ceram. Soc.,
        1954, 37, 107.

(13)   OGINO, K, NISHIWAKI, A, YAMAMOTO, K and HAMA, S. Paper presented at Intl.
        Symp. Phys. Chem. Steelmaking, Toronto, 1982, III-33.

(14)   NAUMAN, J; FOO, G; and ELLIOTT, J F; Extractive Metallurgy of Copper, Chapter
        12, 237.

(15)   GIBBY, R L and BATES, J L; 10th Thermal Conductivity Conference, held
        Newton, Mass., Sept. 1970, IV-7,8. see also BATES, J L, Final Report to
        National Science Foundation, Grant GI-44100 Properties of Molten coal
        slags relating to open cycle MHD, Dec. 1975.

(16)   TAYLOR, R and MILLS, K C; Arch. f. Eisenhuttenw., 1982, 53, 55.

(17)   TAYLOR, R and EDWARDS, R. cited by MILLS, K C and GRIEVESON, P, a paper
        presented at the Centenary Conference 1984, "Perspectives in Metallurgy"
        Sheffield University, July 1984.

(18)   SAITO, A; Bull. Jap. Soc. Mech. Engr., 1980, 23, 1459.

(19)   de CASTRO, C.A.N., L I, S.F.Y., MAITLAND, G.C. and WAKEHAM, W.A, in press
        Intl. J Thermophys. (1984)

(20)   MILLS, K C; POWELL, J S; BRYANT, J W and KEENE, B J, Canad, Metall. Q,
        1981, 20, 93.

(21)   SUSA, M, NAGATA, K and GOTO, K S; Trans. Iron Steel Inst. Japan, 1982
        22 B42.

(22)   MITCHELL, A and WADIER, J F; Canad. Metall. Q. 1981, 20, 373.

(23)   POWELL, J S, and MILLS, K C. Paper to be presented at the Ninth European
        Conference on Thermophysical Properties to be held in Manchester, Sept. 1984.

175

(24)   MILLS, K C. Paper entitled "Estimation of physico-chemical properties
        of coal slags and ashes" to be presented at this conference.

(25)   OSINOVSKIKH, L L, KOCHETOV, N N and BRATCHIKOV, S G; Trudy Urals N-I
        Chern. Met., 1968 (8), 71.

(26)   RUDKIN, R L; Report US AF., ASD-TDR-62-24 II.

(27)   KEENE, B J and MILLS, K C. Arch f Eisenhuttenw. 1981, 52, 311.

(28)   RAFALOVICH, I M and DENISOVA, I A; Fiz. Khim Rasplav. Schlakov, 1970, 181.

(29)   OLUSANYA, A, "The Fundamental Properties of Continuous Casting Fluxes"
        PhD Thesis, Imperial College, London, 1983.

(30)   TAYLOR, R, GRIEVESON, P, TAYLOR, R. Paper entitled "Thermal and Physico-
        chemical properties of continuous-casting slags" to be presented at Ninth
        European Conference on Thermophysical Properties to be held in Manchester
        Sept. 1984.

(31)   NAGATA, K and GOTO, K S. private communication, Tokyo Inst. of Technology,
        1984.

(32)   POWELL, J. S., MILLS, K C unpublished thermal conductivity data on casting
        powders, National Physical Laboratory, 1984.

(33)   OHMIYA, S; TACKE, K H and SCHWERDTFEGER, K; Ironmaking and Steelmaking, 1983,
        10, 24.

(34)   VARGAFTIK, N B and OLESHCHUK, O N; Teploenergetika, 1955, 4, 13.

(35)   ISCHENKO, K D; Met. Kobosokhim, 1970, (21) 82.

(36)   KAWADA, K; Bull. Earthquake Res. Inst., 1966, 44, 1071.

(37)   MURASE, T, and McBIRNEY, A, R; Science, 1970, 170, 16S.

(38)   GRIEVESON, P and BAGHA, S cited by MILLS, K C and GRIEVESON, P in a paper
        presented at the Centenary Conference 1984, "Perspectives in Metallurgy",
        Sheffield University, July 1984

Table I

Reference	No	Slag composition					Sample	Method	Temperature Range °C
		%CaO + MgO	%SiO₂	%FeO	%Fe₂O₃	%Al₂O₃			
Vargaftik (34)	A	12.8	35.9	29.0	5.3	14.3	Liquid, solidified slag; (10 mm) softening point - ca. 1000 °C	Radial heat flow method. Pt and stainless steel crucibles	25 - 1348
	B	3.8	53.5	14.1	6.0	22.7			25 - 1283
	C	2.2	50.8	21.0	-	13.0			25 - 1151
Gibby and Bates (15)			33-61	6-9	6-36	14-32	6 samples, liquid and solid	Laser pulse method	100 - 1600
Taylor (30)		27	34	6.5	4.5% free Fe	22 +5% Na₂O	Glass, (1 mm)	laser pulse method	200 - 950
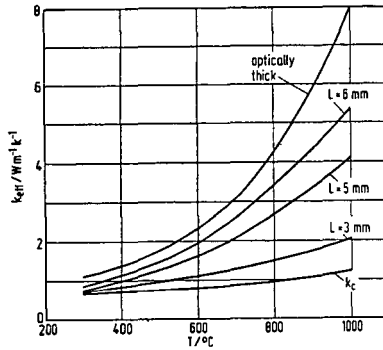
Figure 1.   The dependence of k_{eff} upon the thickness of the sample.
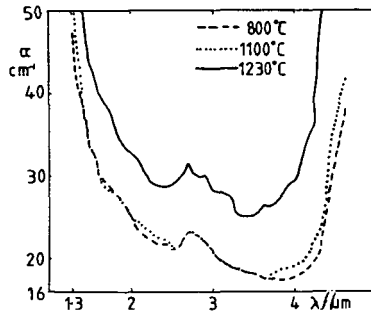
Figure 2.   The wavelength of dependence of a glass containing 67 % SiO_2, 16 % Na_2O + 9 .% (FeO + Fe_2O_3)
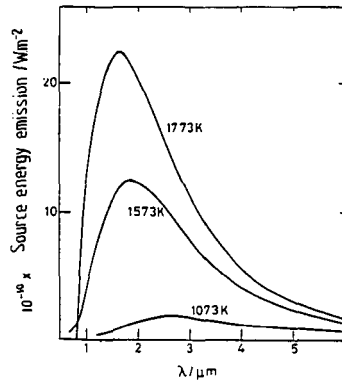
Figure 3.   Wavelength distribution of the source energy emission for a black body.
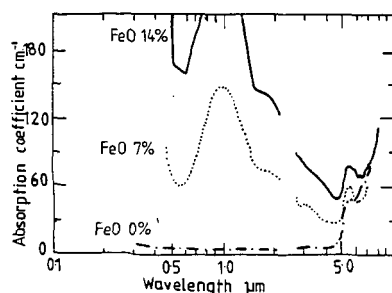
Figure 4.   The absorption spectra at room temperature for slags containing FeO_x + CaO + SiO_2.
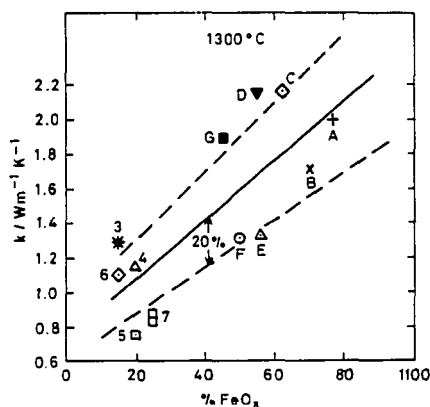
Figure 5.   The thermal conductivity of slags of the system FeO_x + CaO + SiO_2 as a function of the FeO_x content. The letters and numerals refer to the specimen numbers [14].
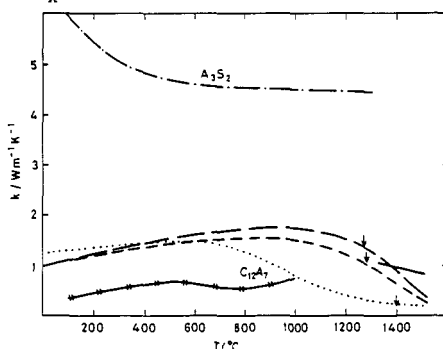
Figure 6.   Thermal conductivities of slags from the system, CaO + Al_2O_3 + SiO_2, ___ . ___, Kingery for $3Al_2O_3.2SiO_2$; ____, Ogino et al ; Susa et al, ... , 50% CaO + 50% Al_2O_3; _ _ _ _ _ , 40% CaO + 40% SiO_2 + 20% Al_2O_3; ___ ___, 25% CaO + 60% SiO_2 + 15% Al_2O_3; ─╫─⊃ Osinovskikh; ▼ , T_{liq}.

179
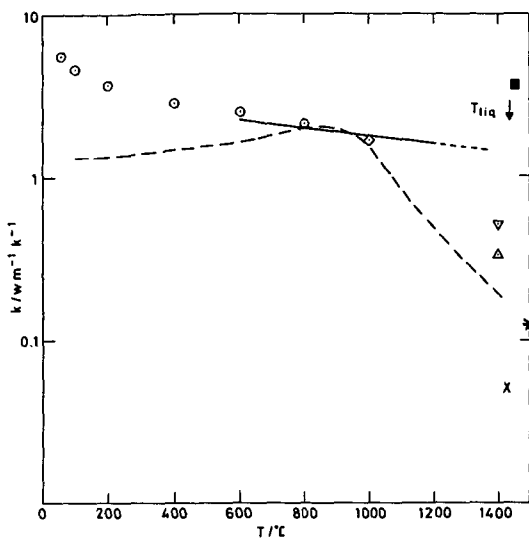
Figure 7.   The thermal conductivity of CaF$_2$ and CaF$_2$- based slags; CaF$_2$; *, Powell; ⊙, Charvat; ●──●─·─·─·─, Taylor; x, Nagata; ■ , Ogino; ▽, Mitchell; CaF$_2$-based slags, ─·─·─·─ , Susa et al; △ , Mitchell.
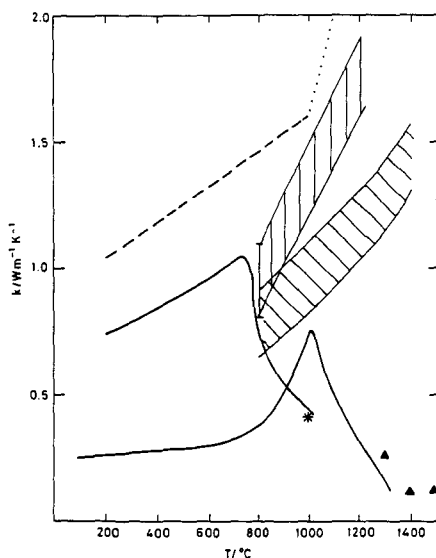
Figure 8.   Thermal conductivity of continuous-casting slags; ─ ─ ─ ─ ;•••• Taylor, and Taylor and Edwards;───── , Nagata; IIII, Ohmiya; *, average k$_c$ value, Ohmiya; ▲ , Powell.

180
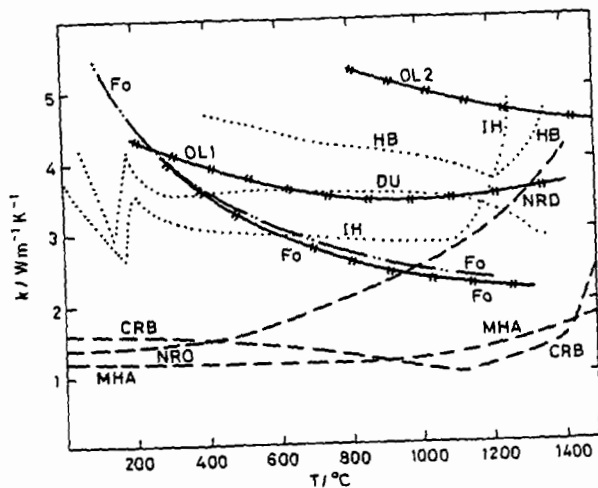
Figure 9. The thermal conductivity of rocks and minerals; — — — , Murase; ——— , Schatz; — ·· — , Kingery; ....., Kawada; the letters refer to samples.
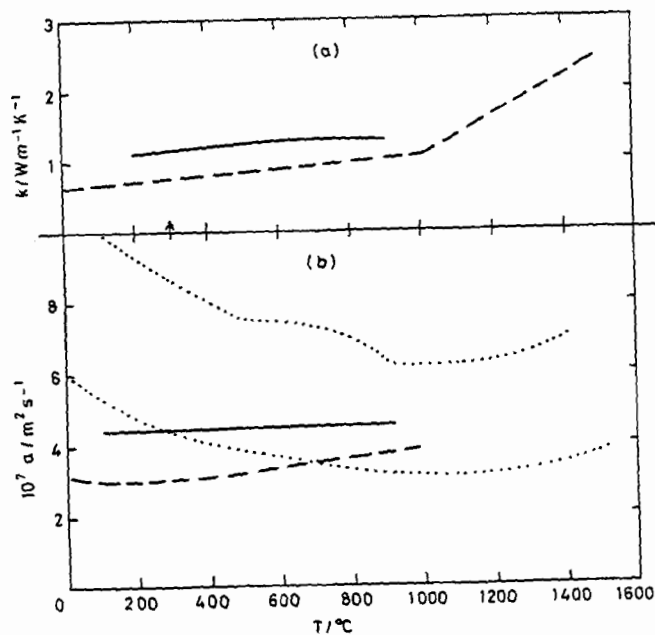

Figure 10. (a) Thermal conductivity (b) thermal diffusivity of coal slags; ———, Taylor; — — —, Vargoftik; ......, upper and lower limits of a values reported by Gibby and Bates.
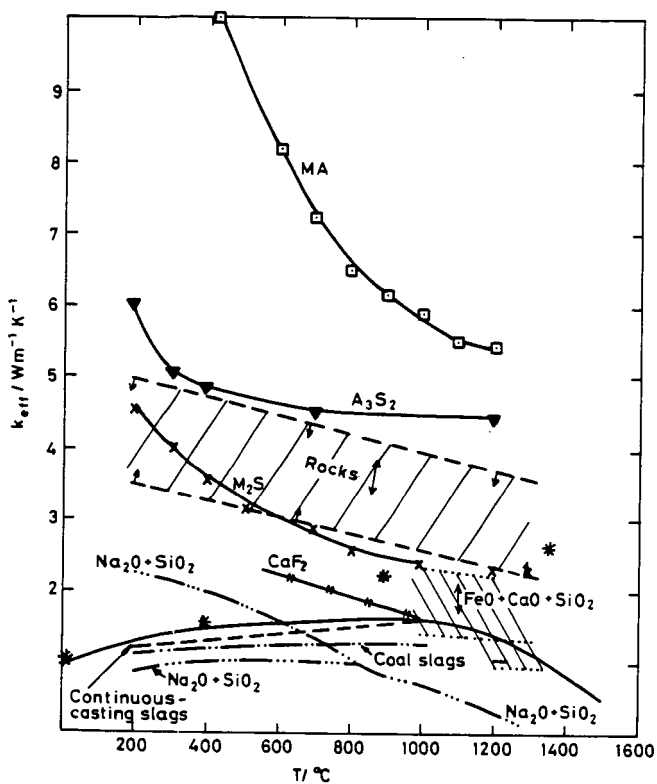
181

Figure 11. The thermal conductivity of various slag systems; ____, $MgO.Al_2O_3$; ____ ., $3Al_2O_3.2SiO_2$; ____, $2MgO.siO_2$; ____, upper and lower limits for data on rocks; ____, CaF_2; ____, data for the $FeO_x + CaO + SiO_2$ system; __ ... __, $Na_2O + SiO_2$ system; ____, $CaO + SiO_2 + Al_2O_3$ system; __ __ __, continuous casting powders; __ .. __, coal slags; *, k_c (glass).